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Open Quantum Systems Coupled to Time-Dependent Classical Environments

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Abstract We investigate the behavior of open quantum systems interacting with classical time-dependent environments. As a simple example, we employ a two-level quantum system, and a thermodynamic oscillator serves as an environment. We analyze how the relationship between parameters of the classical environment and the quantum subsystem changes the evolution. Using the nonlinear thermodynamic master equation, we demonstrate how the energy of the quantum system evolves in time and how feedback effects from a quantum to a classical system influences the dynamics.

Keywords Open quantum systems · Quantum–classical dynamics · Quantum master equation

1 Introduction

In recent years, there has been a growing interest in the physics of open quantum systems. It is of crucial importance for understanding and developing quantum computers [1]. Also, it is widely used in a field of quantum optics [2], transport phenomena [3,4], the theory of photosynthetic complexes [5], and even for the theory of gravity [6].

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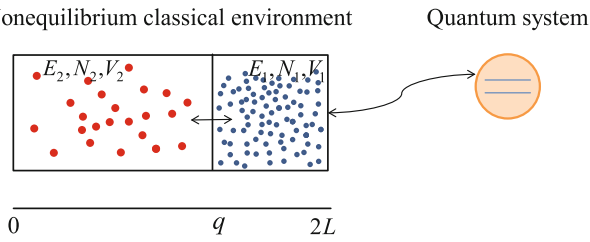

Fig. 1 Model of a quantum system coupled to the time-dependent thermodynamic environment. The two-level quantum system (see Sect. 3) is coupled to the classical environment which consists of two subsystems exchanging heat and volume through a separating wall, which exhibits damped oscillations (see Sect. 3). Initially, the wall has a position q and the size of the classical system is $2L$

The main idea of the theory is very simple: we investigate the dynamics of only the small quantum system of interest, whereas all other degrees of freedom are considered to be an environment, dynamics of which is included implicitly [7]. This approach simplifies calculations a lot, instead of solving the Schrödinger equation for $\sim 10^{27}$ quantum particles, one has to solve a so-called master equation only for few of them, the dynamics of which is the most important.

The problem that arises: how should the environment be treated? Usually it is assumed that the environment consists of an infinite number of quantum harmonic oscillators which do not interact with each other [8]. However, this so-called harmonic bath assumption is still unjustified [9]. The second approach, that is widely used in chemistry (vibrational relaxations in liquids, electron and proton transfer, etc.), deals with the environment as a classical mechanical system [10]. The relaxation rates are calculated with the help of molecular dynamics. This method is very powerful but it requires serious computational calculations. Therefore, we suggest to discuss a more coarse-grained version of the environment and apply methods of modern nonequilibrium thermodynamics [11] to it. We would like to describe a classical environment as a thermodynamic system and investigate the interaction between the quantum system and environment using the nonlinear thermodynamic master equation [12,13].

In this article, we review the nonlinear thermodynamic master equation. With a simple example (Fig. 1), we show how the time-dependence of the environment changes the dynamics of a quantum system. Also, we show how the reaction of the quantum system on the classical environment can be quantified.

The plan of this paper is as follows: in Sect. 2, we describe our tool for investigating quantum–classical dynamics—the nonlinear thermodynamic master equation which describes the evolution of a density matrix of a quantum system. In addition, we formulate a feedback equation which quantifies how the quantum system affects the classical one. In Sect. 3, we describe the two-level quantum system, introduce the most important definitions from quantum mechanics, and show the energy relaxation of a quantum system coupled to a heat bath. Also the thermodynamic oscillator is introduced here and its behavior is analyzed. In Sect. 4, we show the main results for a two-level quantum system coupled to the thermodynamic oscillator. Finally, we discuss our results and offer some conclusions.

2 Nonlinear Thermodynamic Master Equation

Quantum master equations are useful tools for exploring open quantum systems [7,14] and are usually assumed to have a linear form (e.g., Lindblad form [15,16]),

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mathrm{i}\mathcal{L}\rho, \tag{1}$$

where ρ is a density matrix and $\mathcal{L}$ is a superoperator. However, for these equations, two-time correlation functions of two observables calculated with the "quantum regression hypothesis" and the fluctuation–dissipation theorem of the first kind lead to inconsistent results. This suggests that the linear form of the superoperator causes the failure of the "quantum regression hypothesis" for quantum dissipative systems [13,17,18]. Motivated by this fact, Grabert [18] derives a nonlinear master equation which, in the Markovian limit, has the following form

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\rho, H] - \frac{M}{k_\mathrm{B}T_\mathrm{e}}[Q, [Q, H]_\rho] - M[[Q, [Q, \rho]], \tag{2}$$

with a suitable parameter M describing the strength of the dissipation and an observable Q describing the interaction between the quantum subsystem and its infinite quantum environment. The temperature T_e is the only parameter characterizing the state of the environment, which hence acts as a heat bath. For the given operator A and the density matrix ρ, the operator A_ρ is basically the product of A and ρ, but with a compromise between placing ρ to the left or the right of A, $A_\rho = \int_0^1 \rho^\lambda A \rho^{1-\lambda}\mathrm{d}\lambda$.

Recently, the nonlinear master equation was generalized to more complicated classical nonequilibrium systems as environments. Based on purely thermodynamic considerations and a generalization from classical to quantum systems inspired by a geometric formulation of nonequilibrium thermodynamics, the following master equation has been proposed [12,13]:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\rho, H] - \frac{1}{k_\mathrm{B}}[H_e, S_e]_x^Q[Q, [Q, H]_\rho] - [H_e, H_e]_x^Q[Q, [Q, \rho]]. \tag{3}$$

It is important to note that Eq. 3 characterizes a quantum subsystem in contact with an arbitrary classical nonequilibrium system acting as its environment. The first term describes the free evolution generated by the Hamiltonian H, and two other terms have irreversible nature and are caused by coupling of a quantum subsystem to its environment. Whereas the type of coupling is given by the self-adjoint coupling operator Q, the strength of the coupling is expressed in a dissipative bracket $[\bullet, \bullet]_x^Q$ defined as a binary operation on the space of observables for the classical environment. If the equilibrium or nonequilibrium states of the environment are characterized by the state variables x, classical observables are functions or functionals of x which is indicated by the subscript. The classical observables H_e and S_e in Eq. 3 are the energy and the entropy of the environment, respectively. Properties of dissipative brackets are explained in detail in [13]. In our work, we will use the following form of dissipative brackets

$$[A_e, B_e]_x^Q \equiv \frac{\mathrm{d}A_e}{\mathrm{d}H_e} M(T_\mathrm{e}) \frac{\mathrm{d}B_e}{\mathrm{d}H_e}, \tag{4}$$

where $M(T_\mathrm{e})$ is a positive function of a temperature of the environment defined later.

The master equation (Eq. 3) describes the influence of a classical environment on a quantum subsystem. Of course, in response the quantum system also has an influence on its environment. The thermodynamic approach provides a corresponding equation for the evolution of environmental observables [12,13]:

$$\begin{aligned}\frac{\mathrm{d}A_e}{\mathrm{d}t} = \left(\frac{\mathrm{d}A_e}{\mathrm{d}t}\right)_{\mathrm{class}} &- \frac{1}{k_\mathrm{B}}[A_e, S_e]_x^Q \langle [Q, H]; [Q, H] \rangle_\rho \\ &+ [A_e, H_e]_x^Q \langle [Q, [Q, H]] \rangle_\rho,\end{aligned} \tag{5}$$

where canonical correlations are given as

$$\langle A; B \rangle_\rho = \int_0^1 \mathrm{tr}(\rho^\lambda A \rho^{1-\lambda} B) \mathrm{d}\lambda = \mathrm{tr}(A_\rho B). \tag{6}$$

To integrate the nonlinear thermodynamic master equation, we apply the fourth-order Runge–Kutta method according to the procedure described in [13]. Alternatively, a stochastic simulation technique [19] has been developed and could be applied.

3 Models of Quantum System and Classical Environment

3.1 Quantum System

The two-level system is the simplest quantum system and it has two possible states. Many areas of a modern science use this simple model. Examples from quantum chemistry include the electron and proton transfer as well as isomerization reactions. In quantum optics, the model successfully describes nuclear magnetic resonance and spontaneous emission. In quantum computing it is called "qubit," and two states are accordingly denoted $|0\rangle$ and $|1\rangle$.

Any two-dimensional Hermitian matrix of trace one can serve as a density matrix of a two-level system. It is fully defined by three parameters. Hence, one can always write the density matrix of any (mixed or pure) state of the two-level system as

$$\rho = \frac{1 + m_1\sigma_1 + m_2\sigma_2 + m_3\sigma_3}{2} = \frac{1 + \boldsymbol{m} \cdot \boldsymbol{\sigma}}{2}, \tag{7}$$

where σ_i are the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{8}$$

The vector $\boldsymbol{m}$ used to parametrize the density matrix is called the Bloch vector. In addition to conserving the trace equal to one, the density matrix is positive semi-definite, which restricts the length of the Bloch vector to $m \leq 1$, where the equality holds only for the case of a pure state. The expected value for any observable A is given by

$$\langle A \rangle = \mathrm{tr}(\rho A). \tag{9}$$

Therefore, information about the dynamics of the Bloch vector allows one to describe the dynamics of any observable. Hence, our main goal is to find the evolution of $\boldsymbol{m}$. The initial values of the Bloch vector are chosen to be as follows: $m_1 = m_2 = m_3 = 0.1$. First, we establish an evolution equation of a quantum system coupled to a heat bath. As a Hamiltonian of a two-level system, we choose $H = \frac{1}{2}\hbar\omega\sigma_3$, where ω is the angular frequency associated with the energy difference between two levels of the system. Two coupling operators are defined as $Q_j = \sigma_j$, where $j = 1, 2$. The heat bath is characterized by its energy H_e, and the temperature is implied by the thermodynamic relationship $S_e(H_e)$. We assume dissipative brackets of the form,

$$[A_e, B_e]_{H_e}^{Q_j} = \frac{\mathrm{d}A_e}{\mathrm{d}H_e}\gamma\frac{k_\mathrm{B}}{T_\mathrm{e}}\frac{\mathrm{d}B_e}{\mathrm{d}H_e}. \tag{10}$$

In order to work with dimensionless equations, we must normalize all the independent and dependent variables. The most natural characteristic quantity for a given problem is the energy difference between the two levels of the quantum systems ($\hbar\omega$). From now on we set $\hbar = 1$, $\omega = 1$ as well as $k_\mathrm{B} = 1$. This means that we work with dimensionless time ($\omega t \to t$), temperature ($\frac{k_\mathrm{B}T}{\hbar\omega} \to T$), and coupling strength ($\frac{\gamma}{\omega} \to \gamma$). For example, the typical value of ω for semiconducting qubits is of the order of 10 GHz.

The energy of a qubit is proportional to $m_3 = \langle\sigma_3\rangle$ and its relaxation caused by coupling to a heat bath is shown in Fig. 2. For any temperature of the heat bath, there is always a monotonic behavior of the curve. The final value of the energy of a quantum

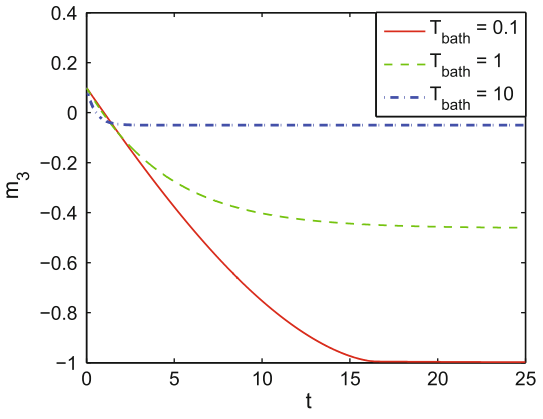

Fig. 2 Relaxation of energy of a two-level quantum system coupled to a heat bath. Temperature changes only the slope of the decay which is always monotonic

system coupled to a heat bath is defined by the Gibbs distribution. The coupling to a heat bath with high temperature ($T_{\text{bath}} = 10$) leads to a mixed state with equally populated ground and excited levels, whereas only the ground state is populated for low temperatures ($T_{\text{bath}} = 0.1$). We always assume weak coupling of a quantum system to the environment and set $\gamma = 0.3$.

3.2 Classical Environment

Now we discuss the simplest possible example of a nonequilibrium thermodynamic environment. It consists of two subsystems exchanging heat and volume through a separating wall of mass m_{wall} (see Fig. 1, left side). We use $x = (q, v, E_1, E_2)$ as variables for the system, where v is the velocity of the wall. For our simulations, we assume that initially the wall is at rest ($v = 0$). Assuming that the subsystems contain the same number of particles, $N_1 = N_2 = N$, we can derive time-evolution equations describing the system [20],

$$\frac{\mathrm{d}q}{\mathrm{d}t} = v, \tag{11}$$

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{1}{m_{\text{wall}}}(p_1 - p_2)A_{\text{c}}, \tag{12}$$

$$\frac{\mathrm{d}E_1}{\mathrm{d}t} = -p_1 A_{\text{c}} v + \alpha\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{13}$$

$$\frac{\mathrm{d}E_2}{\mathrm{d}t} = p_2 A_{\text{c}} v - \alpha\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{14}$$

where the parameter α is responsible for the heat exchange between the two volumes, A_{c} is the cross-section and $2L$ is the length of the container. T_i and p_i are the temperature and the pressure of the subsystem with the energy $E_i (i = 1, 2)$. The energy and the pressure of the subsystems are functions of temperature and volume. In order to show some numerical results, we can apply ideal gas laws and solve the closed system of equations. However, it should be mentioned that Eqs. 11–14 are valid for any real system inside the two volumes. For more complicated models, we cannot obtain the closed system of constitutive equations and should perform simulations.

To make the equation dimensionless, we rescale the length setting L equal to 1 (it is supposed that we have a nanoscale system, $L \sim 10^{-9}$ m). Two dimensionless parameters define the dynamics of the system: the mass of the wall and the heat exchange. Fixing the heat exchange we vary m_{wall} and see two types of solutions of Eqs. 11–14. A heavy mass of the wall leads to monotonic thermalization of the oscillator, whereas a lighter mass allows some damped oscillations (see Fig. 3). The value of the heat exchange defines how fast the system reaches equilibrium.

3.3 Quantum–Classical Coupling

The coupling of a quantum system to the thermodynamic oscillator is shown in Fig. 1. The quantum system interacts only with the subsystem with energy E_1. In addition, the

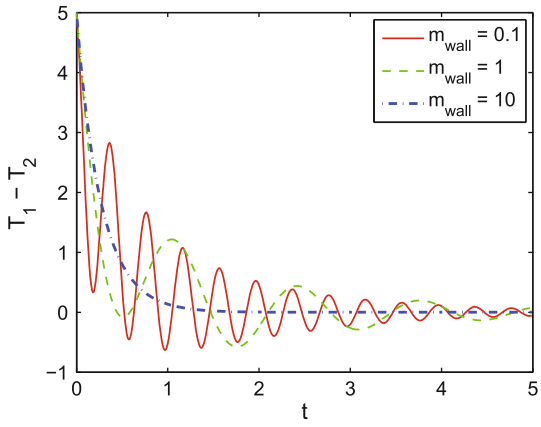

Fig. 3 Thermalization of a thermodynamic oscillator. Because of the exchange of the energy, the two subsystems of the thermodynamic oscillator which initially have different temperatures equilibrate to the same one

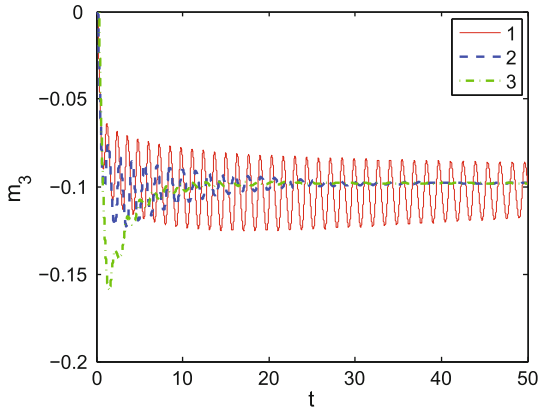

Fig. 4 Energy relaxation of a two-level quantum system coupled to a thermodynamic oscillator. The parameters are: (1) $\alpha = 1,\ T_1 = 10,\ T_2 = 0.1$; (2) $\alpha = 10,\ T_1 = 10,\ T_2 = 0.1$; (3) $\alpha = 1,\ T_1 = 0.1,\ T_2 = 10$; $m_{\text{wall}} = 1$.

second subsystem knows about the quantum system through the wall. The dynamics of our coupled quantum–classical system is defined by the strength of the coupling of the quantum systems to the environment (γ), the heat exchange between subsystems (α), and the mass of the wall (m_{wall}).

4 Results

Figure 4 shows how different dynamics of the quantum subsystem for the case of different parameters can be. Contrary to the case of a quantum system coupled to a heat bath, the energy relaxation shows oscillatory behavior. The frequency and magnitude of oscillations depend on the mass of the wall and they are damped according to the heat exchange between the subsystems. The difference between the lines 1 and 2 shows how different these damped oscillations are. The line 3 shows how a change of the initial temperatures of the subsystems changes the dynamics of the quantum system.

One can argue how the energy of the quantum subsystem can be of the same order (or even larger) than the energy of the environment. However, "The energy of a single

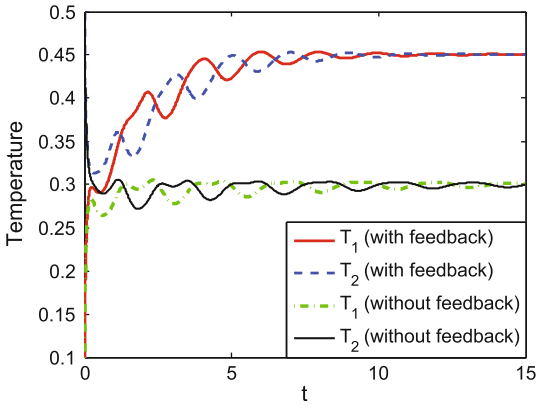

Fig. 5 Effect of the reaction from the quantum system on the thermodynamic oscillator. The parameters are: $m_{\text{wall}} = 0.1,\ \alpha = 1,\ T_1 = 0.1,\ T_2 = 0.5$

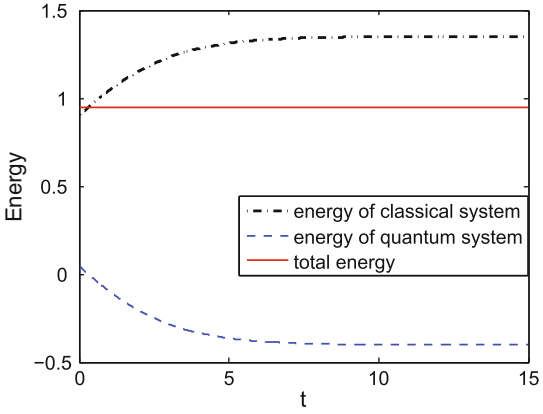

Fig. 6 The conservation of the total energy. The energy of the quantum system and of the environment changes in time, but the total energy is constant. The parameters are: $\alpha = 1,\ m_{\text{wall}} = 0.1,\ T_1 = 0.1,\ T_2 = 0.5$.

quantum of a CO stretch is 10 times what k_{B}T is at room temperature. In effect, shedding a quantum of vibration is equivalent to plunging a red-hot iron into our cold liquid…" [21].

The nonlinear thermodynamic master equation together with the equation which expresses the effect of feedback from a quantum system to a classical environment describes the whole evolution of the closed quantum–classical system. The quantum system affects the environment significantly, as shown in Fig. 5, and its dynamics is changed not only quantitatively but also qualitatively. The initial population of the excited and ground states of a two-level system are not very different (0.55 and 0.45), which means that the effective temperature of a quantum system is high (it is more than 1). Coupling of this system to the subsystem with the temperature $T_1 = 0.1$ causes the flow of the energy from the quantum system to a classical one. Without taking into account the reaction of the quantum system, the equilibrium temperature is incorrect and the law of conservation of energy is violated.

As was mentioned before, the nonlinear thermodynamic master equation guarantees the conservation of the energy and the positivity of the total entropy production. Figures 6 and 7 demonstrate this.

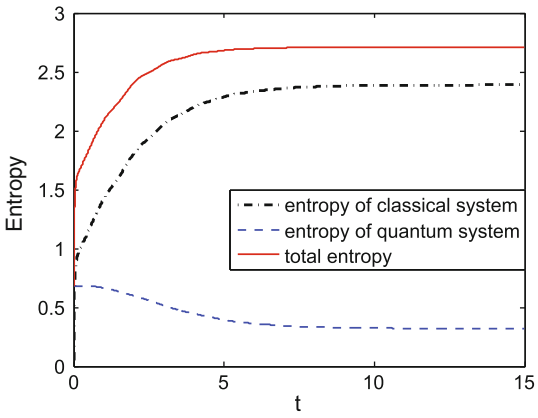

Fig. 7 The entropy of the total system always increases even though the entropy of the quantum and classical system can decrease. The parameters are the same as in Fig. 6

5 Conclusions and Discussion

We have explored the simplest example of interaction between an open quantum system and its classical environment. We show how the interplay between the energies of quantum and classical systems is reflected by the dynamics. The main advantages of the nonlinear thermodynamic master equation (positivity of the entropy production, the conservation of the energy of the total system, and the feedback effect) have been shown.

Finally, we propose more interesting applications of the formalism. The most natural practical application of our approach can be an investigation of *vibrational relaxations in liquids* [22]. In the liquid phase in most cases transitional and rotational degrees of freedom are clearly distinguishable from vibrational ones. Vibrational frequencies are typically larger than the thermal energy which results in a fact that only a few vibrational states are thermally populated. On the other hand, rotational and translational modes have lower frequencies and more states are thermally populated. As a result, classical physics can be applied to describe their dynamics. Thermodynamics and hydrodynamics are the most suitable tools for this task. In addition, it is important to mention that vibrational phase and energy relaxation times can be as short as a few picoseconds, and may thus be comparable to the relaxation times of the environment.

Another application is *electron transfer* [23]. This process is essentially a change in the electronic charge distribution in the molecular systems (solute). Whereas electronic states are assumed to be a quantum system, the surrounding dielectric environment can be considered to be classical. In the Marcus theory of electron transfer, the solvent is taken as a dielectric continuum characterized by a local dielectric function. Methods of classical thermodynamics and electrodynamics can be applied to investigate Debye and non-Debye dielectric relaxation of the environment (solvent). The same description of the environment is valid for *proton transfer* [23].

One more example is a coupling of quantum degrees of freedom to a classical *chaotic system*. During the last decades, this approach to study open quantum system has become very popular. According to our formalism, the environment can be described with the help of thermodynamics of chaotic systems [24].

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